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Japan Patent Office
Kokai Patent Publication No. 156312 - 1987, July 11, 1987

Title of Invention : Polyester Fibers

Patent Application No. 292299 - 1985
Date of Application : December 26, 1985

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Specification

1. Title of Invention
Polyester fibers
2. Claims of the Patent

(1) Polyester fibers which is characterized by consisting of polyester having ethylene naphthalene -2,6 - dicarboxylate as the main repeating unit, limiting viscosity of at least 0.5, strength of over 6.5 g/de, dry heat shrinkage at 180 deg C of less than 3 % and crystal melting point of over 280 deg C.

(2) Polyester fiber described in Claim 1 in which the birefringence is 0.25 - 0.32.

3. Detailed Description of the Invention

(Field of Application in Industry)

This invention is related to polyester fiber which is useful as tire cord, etc.

(Existing Technology)

Poly ethylene terephthalate (hereinafter, this is abbreviated as PET) fiber has various excellent properties and so it is used widely not only for apparel but also for industrial applications. In particular, the PET fiber having high strength as well as good dimensional stability is useful also for industrial applications ; it is used not only in tire applications but also as industrial materials. However,

recently, more and more higher performance is being demanded. For example in the tire cord application, lower shrinkage for improvement of yield at the tire molding, higher modulus for improvement of ride and improvement for fatigue resistance in the application for larger size tire are in demand. On the other hand, as the cord for V belt, higher modulus is needed for maintenance-free use and larger elongation and fatigue resistance are required as the cord for large size, high load, wrapped belts.

From such a view point, if one can obtain polyester cord as the PET fiber which has one step improved excellent lower shrinkage, higher modulus and fatigue resistance, the field of application of PET fiber would increase further because of its superiority in the power of cost competition with other materials. In particular, the PET fiber has inferior modulus and shrinkage property in comparison to rayon fiber and vinylon fiber which have old history. Furthermore, in comparison to the polyamide fiber which has an old history and wide utility, it has very inferior fatigue resistance and so improvement on these is important.

Particularly in Europe, rayon fiber is still used often in tire cord application where PET fiber is almost not used. The reason is that the rayon fiber has very low shrinkage and so the slow cooling process (so called post cure inflation) after the vulcanization of tire is not necessary. In contrast to this, when PET fiber is used, this slow cooling process is necessary and this process requires a very large facility investment and thus there is great resistance to the new installation of this process. Furthermore, the rayon fiber has a very high modulus and, because of this, the tire which uses the rayon fiber cord gives very good ride at high speed.

However, the rayon fibers have very important shortcomings. In other words, it undergoes a large chemical degradation in the presence of moisture and so there is a great degradation caused by the vulcanization; also, because of the water which penetrates in through the cut or crack of tire and the wet heat degradation by the heat generation during running, there is the shortcoming of bringing fatal strength reduction.

Consequently, there is the strong desire for the appearance of tire cord fiber which does not have the above mentioned shortcomings of the rayon fiber and also has the low shrinkage and high modulus comparable to that of rayon fiber.

From the past, on the PET fiber and nylon fiber, various methods of improvement were proposed but they have not been resolved yet.

(The Problem Which the Invention Intends to Solve)

The present inventors focused their attention on the poly ethylene naphthalene -2,6 - dicarboxylate (hereinafter, this is abbreviated as PEN) which has high rigidity of molecular chains and tried making tire cord fiber of this. With the rigidity of its molecular chain, PEN has a high melt viscosity and its fiber has high intrinsic birefringence ; the second order transition point is high and so drawing to a high degree is difficult. Therefore, melting was done at high temperature and melt spinning was conducted by using a heated spinning cylinder at special temperature conditions and then multiple stage drawing at high temperature was conducted and yarn making was conducted successfully. (Kokai JP No. 77116 - 1973). The PEN fiber which is obtained in this way has a high modulus compared to PET fiber and exhibits lower shrinkage and superior heat resistant strength in rubber. Still, it could not reach the low shrinkage comparable to that of rayon.

More of extensive investigation was conducted and, as the result, it was found that the polyester cord of low shrinkage and high modulus comparable to rayon cord and better fatigue resistance than that of rayon cord can be obtained only by using the fiber of specific fiber structure which is obtained by drawing and heat treatment of the crystalline PEN undrawn fiber having very high orientation compared to that of the past. Thus, this invention was arrived at.

(Embodiment of the Invention)

Thus, this invention is related to the polyester fiber which is characterized by consisting of polyester which has ethylene naphthalene -2,6- dicarboxylate as the main repeating unit, a limiting viscosity of at least 0.5, strength of over 6.5 g/de, 180 deg C dry heat shrinkage of less than 3 % and crystal melting point of over 280 deg C.

The polymer which makes up the polyester fiber of this invention is a polyester which contains in the molecular chain over 90 mol % of the repeating unit of ethylene naphthalene -2,6 - dicarboxylate, preferably more than 95 mol %. As for such polyester, poly ethylene -2,6- dicarboxylate is particularly preferred.

In general, PEN can be synthesized by bonding naphthalene - 2,6 - dicarboxylic acid or its ester-forming derivative and ethylene glycol or its ester-forming derivative under

the presence of a catalyst under a suitable reaction condition. Before the completion of polymerization of this polyethylene 2,6 - naphthalate, one or more of suitable, third components are added to synthesize the copolymerized or mixed polyester. As for the suitable third component, examples are the compound having 2 ester-forming functional groups, e.g. the aliphatic dicarboxylic acid such as oxalic acid, succinic acid, adipic acid, sebacic acid, the alicyclic dicarboxylic acid such as cyclo propane dicarboxylic acid, cyclo butane dicarboxylic acid, hexa hydro tere phthalic acid, the aromatic dicarboxylic acid such as ortho phthalic acid, isophthalic acid, terephthalic acid, naphthalene -2,7 - dicarboxylic acid, diphenyl dicarboxylic acid, the carboxylic acid such as diphenyl ether dicarboxylic acid, diphenyl sulfon dicarboxylic acid, diphenoxy ethane dicarboxylic acid, sodium 3,5 - dicarboxy benzene sulfonate, the oxy carboxylic acid such as glycolic acid, p-oxy benzoic acid, p-oxy ethoxy benzoic acid, the oxy compound such as propylene glycol, trimethylene glycol, diethylene glycol, tetra methylene glucol, hexa methylene glucol, neopentyl glycol, p-xylene glycol, 1,4 - cyclo hexane dimethanol, bisphenol A, p,p- diphenoxy sulfon, 1,4 - bis (beta - hydroxy ethoxy) benzene, 2,2 - bis (p - beta - hydroxy ethoxy phenyl) propane, poly oxy alkylene glycol, p-phenylene bis (dimethylol cyclo hexane), or their ester-forming derivatives, the compound of high degree of polymerization derived from the other previously mentioned carboxylic acids, oxy carboxylic acids, oxy compounds or their ester-forming derivative and the compound having one ester-forming functional group, e.g. benzoic acid, benzoyl benzoic acid, benzyl oxy benzoic acid. Also, the compound having 3 or more ester-forming functions groups, e.g. glycerine, penta erythritol, trimethylol propane, can be used in the practically linear range. In the said polyester, the delustering agent such as titanium dioxide or the stabilizer such as phosphoric acid, phosphorous acid and their ester may be contained also. These polymers are obtained by any of the common melt polymerization method and solid phase polymerization method.

The limiting viscosity in this invention is an indicator of knowing the molecular weight of the polymer and it is calculated from the values measured with ortho chloro phenol solution of the polymer at 35 deg C.

For the polyester fiber of this invention, the limiting viscosity needs to be at least 0.5. When the limiting viscosity is less than 0.50, one can not obtain high strength polyester cord. As to its upper limit, there is no need for particular restriction ; however, one with a limiting viscosity of 0.60 - 0.80 is preferred.

The polyester fiber of this invention needs to have a breaking strength of more than 6.5 g/de in addition to the above mentioned specific limiting viscosity. Here, the breaking strength is the value obtained by measuring the load-elongation curve in accordance with JIS L 1017 - 1963 (5.4) and dividing the strength at the time of breaking with the initial denier and the correction of denier due to the elongation is not made. When the breaking strength is less than 6.5 g/de, one can not obtain the high strength polyester cord even if the above said limiting viscosity is satisfied and, in addition, one can not obtain polyester cord of good fatigue resistance.

The polyester fiber of this invention needs to have a 180 deg C dry heat shrinkage of less than 3 % and crystal melting point of over 280 deg C which are based on the specific fiber structure, in addition to the above mentioned limiting viscosity and breaking strength.

Here, the 180 deg C dry heat shrinkage is measured by JIS L 1017 - 1963 *5.12). Also, the crystal melting point is measured at the temperature rising rate of 20 deg C/min using Model DSC-I made by Perkin Elmer Co. and the heat absorption peak value was taken as the crystal melting point.

The polyester fiber of this invention can be made the polyester cord of high modulus and low shrinkage comparable to rayon only by satisfying a 180 deg C dry heat shrinkage of less than 3 % and also a crystal melting point of over 280 deg C simultaneously and it is difficult to achieve the objective of this invention if any one of the characteristic values is lacking.

For the polyester fiber of this invention, it is particularly preferred that the birefringence Δn which indicates the degree of orientation of molecules is 0.25 - 0.32.

Here, Δn is a parameter which indicates the degree of orientation of molecules in the filament. As the dipping liquid, bromo naphthalene was used and the value was determined by the retardation method using Berek compensator. (For the details, see [Lectures on Polymer Experiments, Physical Properties of Polymers II], Kyoritsu Shuppan).

The polyester fiber of this invention is obtained by, for example, the following method. The polyester polymer having ethylene naphthalene -2,6- dicarboxylate as the main component and a limiting viscosity of over 0.60 (preferably 0.6 - 0.95) or the polymer having a limiting viscosity of over 0.4 with the polymerization accelerator being reacted on is

melted and transferred by the common method and this is extruded from the spinning die such that the denier after the drawing would be 1 - 20 de. After the extrusion, it is immediately quenched or is kept at the temperature below the melting point and above the crystallization initiation temperature or it is taken up at a high speed while achieving a delayed cooling to expose it for a certain length of time to the heated atmosphere of a temperature above the melting point and, after this, the said yarn is cooled and solidified. At this time, it is useful to cool and solidify under the following conditions.

$$400 \leq (X \cdot \sqrt{y}) / Q \leq 1900$$

X is the distance from the spinning die face to the surface where the cooling air is blown out and it is less than 450 mm.

y is the length of cooling air blow out zone. 100-500 mm

Q is the rate of cooling air blowing out, 2 - 6 Nm³/min.

After the cooling and solidifying as described above, the oil agent is applied and taking up is done at 1500 m/min or above. The oil application can be done by the common method such as the oiling roller method and spray method. As for the oil, the common oil agent for use in fibers can be used. In the field of fiber application where the adhesion with rubber is regarded important, it is useful to apply the surface treatment agent to impart the adhesion properties.

By selecting such conditions described above at all time, one can obtain crystalline, undrawn fiber which has a limiting viscosity of over 0.50, birefringence of over 0.10 and has a very high degree of orientation compared to the existing known fibers.

Such undrawn fiber can be obtained also by having a draft ratio of the extruded fiber from the spinning die to the take up after the extrusion between 300 - 7000 with the orifice diameter of spinning die in the range of 0.55 - 2.5 mm and controlling the take up speed to 1500 - 6000 m/min. Here the draft ratio is the ratio of the fiber take up speed to the extrusion linear speed (orifice exit speed) of the polymer.

In this invention, the undrawn fiber having the above mentioned properties which was taken at a speed of over 1500 m/min can be drawn in continuation to the spinning or can be drawn in a separate process after first taking up. In the case of drawing in continuation to the spinning, one can conduct the process by the method of previously proposed.

Patent Application 143828 - 1973, Patent Application 88927 - 1982. In the case of first taking up after the spinnign and then drawing, one can conduct the process by the methods of previous proposed Patent Application 102040 - 1969, Patent Application 9717 - 1972, Patent Application 189094 - 1982. The latter drawing method is preferred for minimizing the distortion in drawing or distortion in heat treatment. Thus, in multiple stage drawing, the untreated fiber is preheated for at least 0.5 seconds at the temperature of $T_g+15 - T_g+50$ deg C (here, T_g is the second order transition temperature of the said fiber) and then the first stage drawing is done to less than 75 % of the total draw ratio to make the birefringence 1.2 - 3.3 times that of the undrawn fiber. Next, the said first-stage drawn yarn is given the multiple stage drawing and heat treatment. At this time, if high sgrength is required when made into cord as with the tire reinforcement, the final tension treatment is conducted at the temperature range of fiber melting temperature-50 deg C to melting temperature-110 deg C under a fixed length or under a tension of up to 5.0 % of length, preferably at the fixed length and under a tension of up to 2.5 % for 0.4 - 1.5 seconds.

In the case of using the polyester fiber of this invention as the rubber reinforcing cord, it is preferred to use, for example, the following method. In other words, the said drawn yarn is joined and twisted such that the twist factor $K = T \cdot \sqrt{D}$ (T is the number of twists per 10 cm, D is the denier of the twisted cord) is 900 - 2500 to make twisted cord and the said cord is given the adhesive agent treatment and then the heat treatment at 235 - 270 deg C. At this time it is preferred to conduct the heat treatment under a tension in the range of 1.0 - 2.0 g/den and under the condition where drawing does not occur practically.

The polyester cord obtained from the polyester fiber of this invention exhibits the sum of the intermediate elongation E_i under the load of 2.0 g/de and the dry heat shrinkage S of

$$E_i + S \leq 4.5$$

thus it exhibits high modulus and also very low shrinkage.

Here, the dry heat shrinkage is the value at the temperature of 180 deg C and was measured under JIS L 1017 - 1963 (5.12). In addition, the polyester cord which is due to the method of this invention has a strength of over 5.0 g/de and has better heat resistance and much improved fatigue resistance in rubber structure in comparison to the existing rubber reinforcing poly ethylene terephthalate polyester cord.

(Examples of Application)

In the examples of application, the parts indicate weight parts. Properties of the treated cord were measured by the following methods.

(1) The load - elongation curve was obtained by JIS L 1017 - 1963 (5.4).

(2) The dry heat 180 deg C shrinkage was measured under JIS L 1017 - 1963 (5.12).

(3) In the measurement of heat resistant strength, the greige cord was dipped in the RFL adhesion solution and this was heat treated for 2 minutes at 245 deg C under tension. This treated cord was buried in the vulcanizing mold and accelerated vulcanization was conducted at 170 deg C under a pressure of 50 kg/cm² for 120 minutes. After this, the treated cord was taken out and the strength was measured. 75 % or over was taken as passing. (In common PET cord, this is about 50 - 60 %).

Example of Application 1

In an autoclave attached with a rectification tower, 5000 parts of 2,6 - dimethyl naphthalate, 2600 parts of ethylene glycol, 3.50 parts of calcium acetate - water salt and 1.80 parts of antimony trioxide were charged. This was heated for about 4 hours at 165 - 230 deg C to expel methanol and, after this, 0.840 parts of phosphorous acid was added. Next, the reactant was transferred to a polymerization kettle and the temperature was raised gradually and, at 260 deg C under normal pressure, reaction was conducted for 10 minutes and, at 275 deg C under 20 mmHg, reaction was conducted for 40 minutes. Then, under 290 deg C under the reduced pressure below 0.5 mmHg, polymerization was continued for 100 minutes to obtain the polymer of limiting viscosity 0.55 and end carboxyl group concentration of 28 equivalent / 10⁶ g. After the completion of polymerization, the molten polymer was immediately extruded to make granule (polymer A).

This polymer was heat treated for 3 hours at 190 deg C ; after this, dry nitrogen was passed at a flow rate of 200 ml/min. gram polymer ; this was maintained at 245 deg C for 8 hours to obtain the polymer of limiting viscosity 0.80, end carboxyl concentration of 15 equivalent / 10⁶ g. (Polymer B). Polymer A was melt-transferred at about 300 deg C and polymer B at about 330 deg C and they were extruded from spinning die of 250 holes of hole diameter 0.6 mm ; after this, the cooling air at 25 deg C was blown at 4.0 Nm³ / min over 300 mm to cool and solidify. After this, oiling agent

was applied by oiling roller and then the yarn was taken up at the speed shown in Table 1.

The undrawn fiber thus obtained was fed to the roll which was heated to 125 deg C and, between the drawing roll heated to 195 deg C, the first stage drawing to the draw ratio (DR1) shown in Table 1 was conducted ; after this, over a heated plate at the temperature of 200 deg C of 60 cm length and between the drawing roll heated to 210 deg C, the second stage drawing was conducted to a ratio (DR2) shown in Table 1. After this, it was taken up at 200 m/min through the take up roll at room temperature. Performance of the drawn yarn obtained was as shown in Table 1.

With the drawn yarn obtained, the Z twist of 490 /m was imparted and two of this yarn were joined and the S twist of 490 / m was imparted to make the greige cord of 1000 de x 2 yarn. This greige cord was dipped in the adhesive agent (RFL) solution and heat treatment under tension was conducted at 245 deg C for 2 minutes. The properties of this treated cord were measured and then the cord was buried in rubber and vulcanized to measure the heat resistant strength. The results are also shown in Table 1.

Example of Application 2

In No. 8 of Example of Application 1, the oil was applied after the cooling and solidification ; then, the yarn was taken up at a speed of 3500 m/min. Immediately in continuation to the spinning, the drawing and heat treatment were conducted. Thus, between the take up roll at 3500 m/min and the heated roll at 240 deg C, drawing was done to a ratio of 1.08 by jetting out steam jet heated at 495 deg C ; after this, over the above mentioned heated roll, heat treatment was done while giving 3% controlled shrinkage. After this, taking up was done at 3660 m/min over a cooled roll. The performance of the resulting drawn yarn and the performance of the cord obtained by the same procedure as in Example of Application 1 are shown as Experiment No. 14 in Table 1.

(For Table 1, see the next page with the following translations of the headings).

Table 1.

A. Experiment No. ; B. Polymer ; C-E. Cooling condition ; C-D. Heated cylinder below the die ; C. Length, mm ; D. Temperature, deg C ; E. Distance over which cooling air is blown out, mm ; F. Take up speed, m/min ; G-I. Undrawn yarn ; G. Limiting viscosity ; H. End carboxyl concentration, equiv./ton ; I. Birefringence ; J. Drawing condition ; K-Q. Drawn yarn ; K. Denier, de ; L. Strength, g/de ; M. Elongation, % ;

N. 180 deg C dry shrinkage, % ; O. Crystal melting point, deg C ; Q. Birefringence ; R-U. Treated cord ; R. Strength, kg ; S. 4.5 kg load elongation, % ; T. 180 deg C dry shrinkage, % ; U. Heat resistant strength retention ratio, % ;

+ (Comparative) indicates the comparative example ;
* indicates outside the performance range.

Table 1.

第 1 表																					
A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	
実験品	ポリマ	冷 却 条 件		引取速度 m/分	未 延 伸 糸			延伸条件		延 伸 糸						処 理 コ ー ド					
		口金下保温筒			冷却風の吹出 距離mm	極限粘 度	未端カルボ キシル温度 当量/トン	延伸率	DR 1	DR 2	線度 de	強 度 g/de	伸度 %	180℃ 乾 収 %	結晶点 ℃	延伸 率	強 力 kg	4.5kg 荷 伸 %	180℃ 乾 収 %	耐熱強 力保持 率 %	
		長さmm	温度℃																		
1(比) [†]	A	100	230	180	3000	*0.48	38	0.15	1.21	1.03	1005	*6.3	7.0	2.9	*278	0.27	*10.8	3.5	1.0	*66	
2(比) [†]	B	300	230	440	*1000	0.60	36	*0.07	1.35	1.05	1003	8.8	7.8	*3.6	*272	0.35	15.8	3.4	*1.6	75	
3	B	300	230	440	2000	0.63	34	0.17	1.21	1.02	1001	7.6	7.6	2.2	280	0.30	13.6	3.5	0.8	76	
4(比) [†]	B	300	230	440	3000	0.65	32	0.20	1.05	1.02	1003	*6.2	9.2	2.0	*279	0.25	*10.7	3.6	0.6	*70	
5	B	300	230	440	3000	0.65	32	0.20	1.15	1.02	1001	7.5	7.8	2.2	281	0.31	13.4	3.5	0.7	75	
6	B	300	230	440	3000	0.65	32	0.20	1.17	1.02	995	7.8	7.0	2.5	282	0.32	14.0	3.4	0.8	78	
7	B	300	230	440	4000	0.67	30	0.25	1.09	1.02	1003	6.6	6.5	1.3	285	0.28	11.8	3.5	0.3	30	
8	B	100	230	180	3000	0.58	32	0.23	1.12	1.02	1003	7.2	7.5	1.6	283	0.31	12.9	3.5	0.5	78	
9	B	200	230	280	3000	0.68	32	0.21	1.14	1.02	1001	7.4	7.6	1.8	282	0.31	13.3	3.6	0.6	80	
10	B	200	230	350	3000	0.67	33	0.18	1.16	1.02	1004	7.6	7.7	2.0	281	0.32	13.8	3.4	0.8	82	
11	B	200	300	350	3000	0.67	33	0.15	1.20	1.02	1003	7.8	7.4	2.4	280	0.32	14.2	3.5	0.9	82	
12	B	200	350	350	3000	0.66	34	0.13	1.24	1.02	1005	8.0	7.3	2.8	280	0.32	14.3	3.4	1.1	80	
13(比) [†]	B	300	350	440	3000	0.64	36	*0.09	1.20	1.02	1006	8.5	7.2	*3.3	*275	0.35	15.2	3.5	*1.2	75	
14	B	100	230	180	3500	0.71	30	0.24	1.08	0.97	1009	6.7	7.3	2.6	284	0.30	12.0	3.5	0.6	80	

†(比) は比較例を示す。 *は性能範囲外を示す。

TELJ ★ F01 87-232152/33 ★J6 2156-312-A
Polyester fibre used pref. for mfr. of tyre cord - comprises ethylene
naphthalene-2,6-di:carboxylate as repeat unit, and has defined
properties

TELJIN KK 26.12.85-JP-292299

A23 (11.07.87) D01f-06/62

26.12.85 as 292299 (84KM)

Fibre consists of polyester having ethylene
naphthalene-2,6-dicarboxylate as main repeat unit and limiting
viscosity of at least 0.5. The fibre has tenacity of more than 6.5 g/de.
heat shrinkage at 180 deg.C of less than 3% and crystal m.pt. of
higher than 280 deg.C. The polyester fibre has double refractive
index 0.25-0.32.

The polyester fibre consists of more than 90 mol.% of ethylene
naphthalene-2,6-dicarboxylate as repeat unit and contains third
component consisting of aliphatic dicarboxylic acid, alicyclic
dicarboxylic acid, aromatic dicarboxylic acid, glycolic acid, p-
oxybenzoic acid and propylene glycol, tetramethylene glycol,
hexamethylene glycol, neopentyl glycol or o-xylene glycol, before
completion of polymerisation of naphthalene-2,6-dicarboxylic acid
or its deriv. and ethylene glycol or its deriv. (6pp Dwg.No.0/0)

C87-098048